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Collective electron ferromagnetism

III. Nickel and nickel-copper alloys

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The collective electron treatment of ferromagnetism (Stoner 1938*a*, 1939) is applied to the magnetic and thermal properties of nickel and nickel-copper alloys. In §1 a brief description is given of the theoretical background, together with the necessary extensions of the basic treatment, in particular so as to cover the effects of the overlap of the electronic *d* and *s* energy bands. With simplifying assumptions regarding the effect of alloying on the electronic structure, and using a limited range of observational data, estimates are obtained of the variation of the specifying parameters, band width and interchange interaction, for nickel-copper alloys, over a wide range of composition (§2). A discussion is given in §3 of the dependence of the electron distribution on temperature. Calculations are carried out of the variation of the number of holes in the *d* band, due to the temperature redistribution of electrons between the bands (transfer effect). Other temperature effects, such as the variation of the specifying parameters due to thermal expansion, are briefly discussed, though they are not included in the main treatment (§§1 and 4).

The treatment is applied to the temperature variation of susceptibility above the Curie point (§4). For nickel-rich alloys satisfactory agreement is obtained with experimental results (figures 10, 11 and 12). For copper-rich alloys the observed high-temperature increase of susceptibility is well explained (figure 13), but no interpretation can be given of the observed low-temperature variation. It is suggested that this may be due to inhomogeneities in composition.

A discussion is given in §5 of the bearing of the treatment on the electronic heat at high temperatures. Comparison is made with the relevant experimental results for nickel above the Curie point. Application is also made to the low-temperature electronic heat of nickel-copper alloys (§5). The general character of the variation of the electronic heat with composition is covered satisfactorily in the nickel-rich regions, but in the copper-rich regions discrepancies occur, similar to those for the low-temperature susceptibility (§4).

In §6 a brief account is given of the results of a preliminary analysis of the magnetic properties of nickel alloys other than those with copper.

1. INTRODUCTION

The magnetic and thermal properties of ferromagnetic metals have been treated on a collective electron basis by Stoner in two papers published just before the war (1938*a*, 1939). In these papers (which will be referred to as I and II) the characteristics associated with electrons (or 'holes') in a single-energy band of 'standard' form, and subject to interchange interaction effects, were obtained with numerical precision for effectively the complete range of values of the specifying parameters and of the temperature. The application of the results to the interpretation of the properties of particular ferromagnetics was discussed in only a preliminary way, but this discussion, together with earlier work on the specific heat of nickel (Stoner 1936, 1938*b*) and a short paper on the temperature variation of susceptibility above the Curie point (Stoner 1938*c*), showed clearly the co-ordinating value of the treatment. It has since been discussed, in relation to the general background, by Van Vleck (1945) and Stoner (1948).

In the present paper the application to nickel and nickel-copper alloys is considered in detail. This has involved, on the one hand, a critical analysis of the experimental results, and, on the other, an extension of the theoretical treatment, in particular so as to cover in a precise way the effects of band overlap. The nickel-

copper alloys have been chosen for detailed consideration, partly because extensive experimental data are available, and partly because the general issues are less likely to be confused by complicating factors than for most other ferromagnetic alloys. The crystal structure of the two constituent metals is the same, and there is no change of phase over the whole composition range. Moreover, the electronic structures are similar, and the assumption, in the present treatment, of a standard band form, in which the energy density of states is proportional to the square root of the energy (measured from an appropriate zero), receives some justification, as a reasonable approximation in these metals, from such calculations on band forms as have been made. There are, however, very great difficulties in carrying out detailed accurate theoretical calculations of band forms in metals and alloys. For this reason, part of the value of a survey of the present kind is that it enables an assessment to be made of the applicability of the simplifying assumptions represented by the premises of the precise deductive treatment. Further, it may suggest, in particular cases, the relative importance of the various uncertain factors, which, for obvious reasons, are deliberately excluded from consideration in the basic theoretical treatment.

(a) *Theoretical background*

The detailed numerical results of the statistical treatment which has been developed apply to electrons distributed in energy bands of 'standard' form. For nickel and copper the two important bands are those usually denoted by the terms '4s band' (since here atomic *s* functions predominate) and '3d band' (in which atomic *d* functions predominate). The work of Mott (1935), Krutter (1935) and Slater (1936) indicates that for these two metals the energy bands overlap strongly, the distribution of the electrons between the two bands being determined by the amount of overlapping. In the copper atom there are ten *d* electrons and one *s* electron outside closed shells. The *d* band in metallic copper is thus full at absolute zero, and the half-filled *s* band gives rise to the conductivity and other electronic properties of the metal. Nickel contains one electron per atom less than copper. The magnetic properties of its alloys indicate that, owing to the band overlap, the outermost electrons in nickel are so distributed that at absolute zero the *d* band contains approximately 9.4 electrons, and the *s* band 0.6 electrons per atom. The *d* band thus contains 0.6 holes per atom, which, owing to the much greater energy density of states, give rise to many of the characteristic properties of the metal, such as its high electronic heat, and, in conjunction with the positive interchange interaction, to the ferromagnetic properties. (The foregoing results as to the number of holes in the *d* band of nickel strictly apply only to 0° K. The redistribution of electrons between the bands at higher temperatures is discussed below, and, more fully, in § 3.)

Apart from the number of electrons, the characteristics of a single band are completely specified, in Stoner's treatment, by two parameters, ϵ_0 and θ' , giving measures of the band width and the interchange interaction respectively. It is necessary to consider the choice of parameters for a similar specification of two overlapping bands.

(i) *Band width.* For single bands of standard form the specification required is provided by the maximum Fermi energy at absolute zero, measured from the

bottom of the band (or, if holes are relevant, from the top of the band). With the band structure assumed for copper and nickel, a value is required not only of the energy width of the unoccupied part of the d band, ϵ_{0d} , but also of the occupied part of the s band, ϵ_{0s} (see figure 1). Values of these two quantities may be estimated for nickel from observational data, and calculated for nickel-copper alloys by methods indicated in § 2.

(ii) *Interchange interaction.* In Stoner's treatment the interchange interaction coefficient, θ' , is such that $2k\theta'\zeta$ is the energy difference for spins parallel and anti-parallel to the resultant spin, ζ being the relative magnetization, i.e. the ratio of the resultant spin per atom to the maximum possible, when parallelism is complete. The simple, though justifiable, assumption is made that the exchange effects introduce a term into the expression for internal energy which is proportional to ζ^2 . Thus $k\theta'$ is formally equivalent to the Weiss molecular field coefficient. In calculating values of θ' for nickel-copper alloys, exchange effects between d electrons only are considered, those between s electrons being neglected. It is to be noted that it is only exchange effects corresponding to a positive interchange interaction integral in the two-atom problem which are relevant; negative interaction effects are, in effect, included in the form assumed for the bands. Neglect of a positive exchange effect with s electrons is justifiable, not only because any such interaction is likely to be weak with s -type wave functions, but also because the factor determining the effect of the exchange forces is the ratio $k\theta'/\epsilon_0$, and the band width ϵ_{0s} is much larger than ϵ_{0d} (cf. § 2). Possible positive exchange effects between d and s electrons have also been neglected, so that the parameter specifying the interchange interaction for two overlapping bands of the present type may be taken equal to that applicable to a single d band.

No satisfactory method of estimating θ' theoretically has yet been developed. The only attempt that has been made (Slater 1936) suffers from serious oversimplification (cf. Van Vleck 1945; Stoner 1948). Since in the course of the present work it was necessary to obtain approximate values of θ' not only for nickel but also for nickel-copper alloys, resort was made to a simple empirical method, to be described in § 2. This method also permitted an examination to be made of the saturation properties of the alloys at absolute zero. As shown in I, the occurrence of positive interchange interaction does not necessarily imply complete saturation, or parallelism of spins, at absolute zero, where, in the range

$$\frac{2}{3} < k\theta'/\epsilon_{0d} < 2^{-\frac{1}{2}}, \quad (1.1)$$

the relative magnetization, ζ_0 , though positive, is less than unity. The condition (1.1) holds for the nickel-rich alloys, and calculations may be carried out to determine how the relative magnetization at absolute zero depends on the copper concentration.

(b) *Application to nickel-copper alloys*

Values of the characteristic quantities, band width and interchange interaction, can be estimated for the alloys only on the basis of what is essentially an assumption as to the effect on the electron distribution of dissolving copper in nickel. It was first suggested by Mott (1935) that in the alloys the additional s electrons provided by

the copper are distributed among available states in the d band. The question as to whether the holes in the d band are to be regarded as being associated equally with all the atoms or only with the nickel atoms has been considered by Niessen (1939), following on earlier work by Hironé (1938). Niessen suggests that in nickel-copper alloys the d band is common to all the atoms. As stated in § 2, however, Niessen's argument is based on the assumption of the equality of the Curie temperature, θ , with the interchange interaction temperature, θ' , and may well be erroneous. In any case, the effect of alloying is that, with an increasing copper concentration, the Fermi limit at absolute zero, common to both bands, shifts to energy levels which are unfilled in pure nickel. The number of holes per atom in the d band decreases, and the number of electrons per atom in the s band increases. The consequences of this hypothesis can be readily developed, provided it is further assumed that, although the addition of copper atoms to nickel affects the electron distribution, it leaves the shape and position of the two bands unaltered. This assumption, the simplest possible, is adopted provisionally, and, until more accurate methods have been developed for carrying out the fundamental theoretical calculations required, its appropriateness can be tested only by a comparison with the experimental results of the consequences to which it leads. The magnetic data on the variation of Curie temperature and saturation moment with copper concentration, in particular, serve to bear out the simple assumption to a remarkable degree, at least for low copper concentrations (cf. § 2). Even for alloys of nickel with other metals, such as zinc, aluminium and silicon, where the assumption might be expected to be much further from the truth, the magnetic data indicate a very similar behaviour (cf. § 6).

On the basis of these simple and definite assumptions as to the effect of alloying on the electron distribution, it is possible to relate the number of holes in the d band at absolute zero to the copper concentration, c (cf. § 2). As already indicated, estimates may also be made of the interchange interaction coefficient, θ' , and of the relative magnetization at absolute zero. It then remains to investigate the behaviour of the alloys as the temperature is raised. The most immediate problem, that of the variation of the spontaneous magnetization below, and of the susceptibility above the Curie point, has been considered in I, and the variation of the electronic energy and specific heat in II. The treatment given is, however, strictly applicable only to a single isolated band. When there are two overlapping bands, as in nickel, a transfer of electrons from the d band to the s band takes place with increase in temperature. This effect may greatly modify the conclusions applicable to a single band with a fixed number of electrons. A method of treating this effect has so far been given only for pure nickel (Wohlfarth 1948), and it is necessary to extend the treatment to cover the alloys (cf. § 3).

It may be noted here that there are at least two further temperature-dependent factors which may influence the magnetic and thermal properties of the alloys. As to the first of these, the variation of band structure with temperature owing to thermal expansion, no more than a qualitative discussion can be given at present. A full treatment would involve a complete examination of the energy bands, the work of Krutter (1935) being taken as a starting point. The second factor is the

indirect dependence on temperature of the interchange interaction. A tentative discussion of this effect has been given by Néel (1940), who considers the effect of thermal expansion and atomic oscillations on the effective interatomic distance and hence on the molecular field coefficient. As indicated in § 4, a temperature dependence of interchange interaction is also caused by the temperature variation of the number of holes in the d band, owing to the electron transfer. To the approximation used here it was felt that the neglect of these factors could be justified. It was found, however, that the agreement between theory and experiment could be improved in some cases by making some allowance for them (cf. § 4).

(c) *Experimental results*

With the theoretical background outlined it is possible to give a detailed co-ordinating scheme for a number of distinct physical properties of nickel and nickel-copper alloys. Their magnetic behaviour above the Curie point is discussed in § 4. The experimental results, due to Sucksmith & Pearce (1938) and Fallot (1944) (nickel), and to Wheeler (1939) and Kaufmann & Starr (1943) (nickel-copper), are unusually complete, and their general characteristics may be interpreted fairly satisfactorily. The peculiar susceptibility results which Kaufmann & Starr obtained for copper-rich alloys are only partly explicable, and for a full interpretation the present treatment requires further extension. The thermal properties of nickel and the alloys are discussed in § 5, following on the earlier work of Stoner (1936, 1938*b*). It is shown that the low-temperature specific heat results of Keesom & Kurelmeyer (1940) are in qualitative agreement with those predicted by the present treatment. It is also shown that the electron transfer between the bands will have a marked effect on the high-temperature electronic heat, but the relevant experimental data (Klinkhardt 1927; Sykes & Wilkinson 1938) are too meagre to allow of a satisfactory comparison. The thermionic properties of nickel have been discussed elsewhere (Wohlfarth 1948). In § 6 a brief account is given of the magnetic properties of alloys of nickel with metals other than copper.

It will be noted that this list does not cover all the relevant physical properties of nickel and its alloys, the most obvious omission being the behaviour of these substances below the Curie point. The omission has been made deliberately, since it was felt that the present treatment would be inadequate to cover magnetic and thermal properties other than those mentioned. The variation of spontaneous magnetization with temperature, in particular, would require a fuller consideration of effects, such as 'fluctuations of the molecular field' (Néel 1940), which lie outside the scope of the present paper.

2. BAND WIDTHS AND INTERCHANGE INTERACTION COEFFICIENTS

The idealized band form, which has been assumed for nickel, is shown schematically in figure 1. For a quantitative numerical treatment of actual physical properties it is necessary first to obtain estimates of the band widths, ϵ_{0s} and ϵ_{0d} , and of interchange interaction coefficients, for nickel and nickel-copper alloys.

(a) Band widths

A value of ϵ_{0d} for nickel is derived from observational data. From the relation between ϵ_{0d} and the low-temperature electronic heat a value of about 2.4×10^3 °K is obtained for the degeneracy temperature ϵ_{0d}/k , account being taken of the contribution to electronic heat from the s electrons and of that arising from the electron transfer between the bands (cf. § 5). An independent estimate may be obtained from the Curie temperature and the high-temperature susceptibility of nickel. The discussion in § 4 indicates that for nickel the relative magnetization at absolute zero, ζ_0 , is just equal to unity, and the degeneracy temperature deduced is about 1.6×10^3 °K. The discrepancy between these two estimates may be attributed to deviations of the band structure from that presupposed, to effects of thermal expansion, and to other factors not included in the treatment. For the numerical work a value for $\epsilon_{0d}/k = 2 \times 10^3$ °K, corresponding to $\epsilon_{0d} = 0.17$ eV, has been adopted, except where the use of the 'high-temperature' value is necessitated by the basic theoretical treatment (cf. § 5).

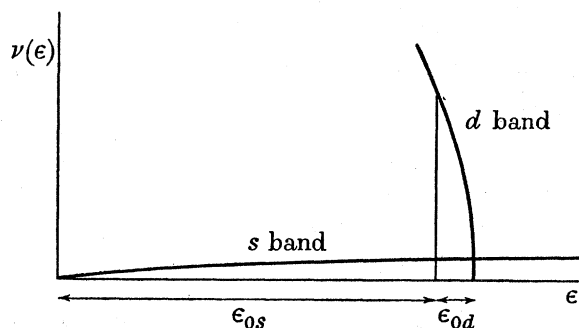


FIGURE 1. Band structure near the Fermi limit for nickel. ϵ , electronic energy. $\nu(\epsilon)$, energy density of states: $\nu(\epsilon) \propto \epsilon^{\frac{1}{2}}$. ϵ_{0s} , occupied width of s band; ϵ_{0d} , unoccupied width of d band, both at absolute zero, when number of 'particles' in either band equals 0.6 per atom.

The occupied width of the s band, ϵ_{0s} , may be estimated for nickel on the assumption that the energy distribution of the s electrons does not differ significantly, over the range covered, from that of free electrons, as for sodium, and, with fair approximation, for copper. The value obtained in this way, $\epsilon_{0s}/k = 6 \times 10^4$ °K, is, however, almost certainly an overestimate.

The value of the ratio of the band widths,

$$r_0 = \epsilon_{0s}/\epsilon_{0d},$$

is of importance in connexion with the distribution of electrons between the bands, the transfer effect being more pronounced the smaller r_0 (cf. § 3), but, owing to the uncertainties in the values of ϵ_{0s} and ϵ_{0d} , it is not possible to make a precise estimate of the ratio. In order to bring out clearly the general effect of the s band on the physical properties, the main calculations to be described have been made for an r_0 value of 10, which must be regarded as a lower limit. In most instances it is easy to see what would be the effect of a higher value of r_0 . In the limit, $r_0 \rightarrow \infty$, the model

corresponds to a single isolated d band, to which the results obtained in I and II are immediately applicable.

Using a value of the band width ratio for nickel, r_0 , equal to 10, with the simplifying assumptions regarding the effect of alloying (cf. § 1), precise calculations may be made of the band widths, the number of holes in the d band and related quantities, as dependent on copper concentration, for nickel-copper alloys.

For a given fractional atomic concentration of copper, c , let the fraction of electrons entering the d band at absolute zero be c_d , that entering the s band c_s . Also let the number of holes per atom in the d band be N_{0d} , and the number of electrons per atom in the s band N_{0s} , both at 0° K.

$$\text{Then} \quad N_{0d} = 0.6 - c_d, \quad N_{0s} = 0.6 + c_s, \quad (2.1)$$

$$\text{where} \quad c_d + c_s = c. \quad (2.2)$$

Further, let $(\epsilon_{0d})_c$ and $(\epsilon_{0d})_0$ be the unoccupied widths of the d band at absolute zero for an alloy of copper concentration c and for pure nickel respectively, and let $(\epsilon_{0s})_c$ and $(\epsilon_{0s})_0$ be the occupied widths of the s band. Since the density of states for both bands is taken to be proportional to the square root of the energy, integration gives

$$N_{0d} = 0.6\{(\epsilon_{0d})_c/(\epsilon_{0d})_0\}^{\frac{3}{2}}, \quad N_{0s} = 0.6\{(\epsilon_{0s})_c/(\epsilon_{0s})_0\}^{\frac{3}{2}}. \quad (2.3)$$

Since at absolute zero the Fermi limits for the two bands coincide,

$$(\epsilon_{0d})_c + (\epsilon_{0s})_c = (\epsilon_{0d})_0 + (\epsilon_{0s})_0. \quad (2.4)$$

It follows from equations (2.1) to (2.4) that

$$(N_{0d})^{\frac{2}{3}} + r_0(c + N_{0d})^{\frac{2}{3}} = (0.6)^{\frac{2}{3}}(1 + r_0), \quad (2.5)$$

determining the number of holes in the d band as a function of the copper concentration. Values of the band widths, $(\epsilon_{0d})_c$ and $(\epsilon_{0s})_c$, and of the number of electrons in the s band, N_{0s} , may then be derived from the preceding equations. The relation (2.5) shows that for a certain copper concentration, say $c_{\text{crit.}}$, the d band is completely filled. From (2.5)

$$c_{\text{crit.}} = 0.6\{(1 + r_0)/r_0\}^{\frac{3}{2}},$$

giving $c_{\text{crit.}} = 0.6922$ for $r_0 = 10$, and 0.6 for $r_0 \rightarrow \infty$, corresponding to an isolated d band. For $c < c_{\text{crit.}}$, the additional electrons enter both bands, while for $c \geq c_{\text{crit.}}$, they enter the s band only, at absolute zero. Calculations of N_{0d} and N_{0s} , for $r_0 = 10$, have been carried out, using equation (2.5) and employing a 'balancing' method of solution. The results are shown in figure 2. The physical bearing of these results is discussed in §§ 3, 4 and 5.

(b) Interchange interaction coefficients

The dependence of interchange interaction coefficients and related quantities on copper concentration may be estimated from experimental values of the Curie temperatures for nickel-copper alloys. Observed value of θ , due to Alder (1916), Krupkowski (1929), Marian (1937) and Wheeler (1939), are shown in figure 3.

For alloys with $c < 0.4$ the observed values fall roughly on a straight line, given by

$$\theta = 631(1 - c/0.6). \quad (2.6)$$

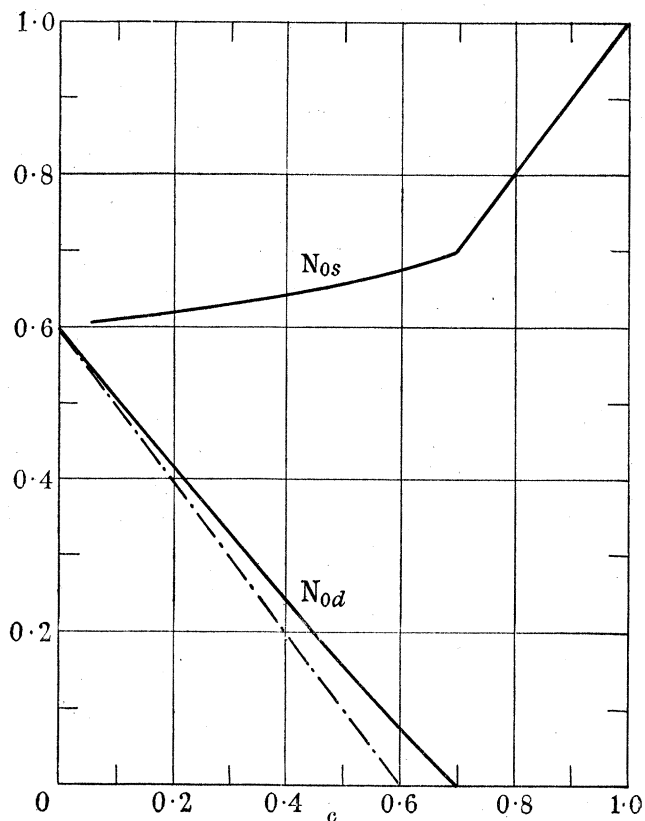


FIGURE 2. Electron distribution at absolute zero for nickel-copper alloys. c , fractional atomic concentration of copper. N_{0d} , holes per atom in the d band. N_{0s} , electrons per atom in the s band. Full curves, $r_0 = 10$, where $r_0 = (\epsilon_{0s})_0/(\epsilon_{0d})_0$. Broken curve, $r_0 \rightarrow \infty$.

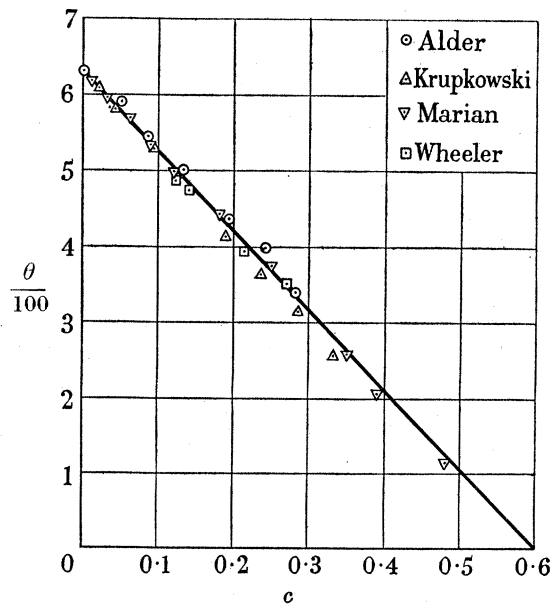


FIGURE 3. Experimental values of the ferromagnetic Curie temperatures for nickel-copper alloys. c , fractional atomic concentration of copper. θ , Curie temperature ($^{\circ}\text{K}$).

For higher copper concentrations the ordinary methods of Curie point determination are unsatisfactory, since, owing to inhomogeneities of the alloys, the temperature at which the spontaneous magnetization vanishes is not clearly defined (Marian 1937). For the purpose of the present treatment the relation (2.6) is, however, assumed to hold for all values of copper concentration. Calculated values of interchange interaction coefficients are thus uncertain for $c > 0.4$.

Use of (2.6) enables θ' values to be calculated for the alloys, provided the value is known for pure nickel. As shown in § 4 the experimental susceptibility results indicate that for nickel the relative magnetization at absolute zero, ζ_0 , is just equal to unity, the value of $k\theta'/\epsilon_{0d}$ being equal to the critical value, $2^{-\frac{1}{2}}$, given in (1.1). Hence, from I (table III),

$$\theta'/\theta = 1.952,$$

giving $\theta' = 1232^\circ \text{K}$, i.e. $k\theta' = 0.106 \text{ eV}$ for nickel. Calculations of θ' as a function of the Curie temperature may be carried out, using the relations (cf. I, (3.9))

$$\left. \begin{aligned} \frac{k\theta'}{\epsilon_{0d}} &= \frac{k\theta}{\epsilon_{0d}} \frac{F(\eta)}{F'(\eta)}, \\ \text{with } F(\eta) &= \frac{2}{3}(k\theta/\epsilon_{0d})^{-\frac{1}{2}}, \quad F'(\eta) = (d/d\eta) F(\eta). \end{aligned} \right\} \quad (2.7)$$

In these relations $F(\eta)$ is the standard Fermi-Dirac integral, η being the statistical parameter. The relations apply strictly only to 'particles' distributed in a single isolated band. Owing to the electron transfer between the d and s bands in nickel and the alloys, the number of holes and the unoccupied energy width of the d band increase with temperature. The necessary correction to θ' is, however, negligible, since, at temperatures corresponding to the Curie point, the transfer effect is relatively small (cf. § 3).

Values of $k\theta'/\epsilon_{0d}$ as dependent on $k\theta/\epsilon_{0d}$ are given in I (table III) for equi-spaced values of the argument. Intermediate values are readily computed by direct interpolation or by means of a series expansion. The dependence of θ' on the copper concentration may thus be obtained, using relations (2.1) to (2.7). The final results are given in table 1 and also in figure 4. The values of the interchange interaction parameters so derived may be used to calculate the variation of ζ_0 , using the relation (cf. I (5.10))

$$2\zeta_0(k\theta'/\epsilon_{0d}) = \{(1 + \zeta_0)^{\frac{1}{2}} - (1 - \zeta_0)^{\frac{1}{2}}\}. \quad (2.8)$$

This equation was solved by a 'balancing' method, by adjusting values of ζ_0 until the two sides of (2.8) are equal. The results are given in table 1 and in figure 5, which also includes a curve giving the dependence on copper concentration of the effective number of magnetic 'carriers' per atom, denoted by n_{0d} . This is given by

$$n_{0d} = \zeta_0 N_{0d}, \quad (2.9)$$

and is proportional to the absolute saturation moment σ_0 . Figure 4 shows that for nickel-copper alloys the ratio θ'/θ increases, with copper concentration, from the value 1.95 for pure nickel. This value may be compared with the value 1.53 obtained by Slater (1936) by a different method. The general conclusion, that θ' is greater than, and not proportional to, the Curie temperature, is independent of the particular band form assumed. The usual method of estimating the exchange energy

from the Curie temperature, which is based, in effect, on the assumption that $\theta' = \theta$, may therefore lead to serious errors. The assumption is made, for example, in Niessen's discussion of nickel alloys (1939).

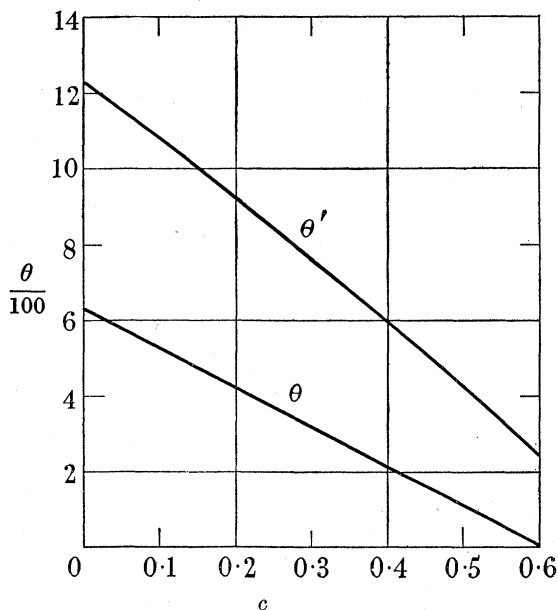


FIGURE 4. Variation of interchange interaction coefficients for nickel-copper alloys. c , fractional atomic concentration of copper. θ , Curie temperature, $^{\circ}\text{K}$ (cf. equation (2.6) and figure 3). θ' , interchange interaction coefficient, $^{\circ}\text{K}$.

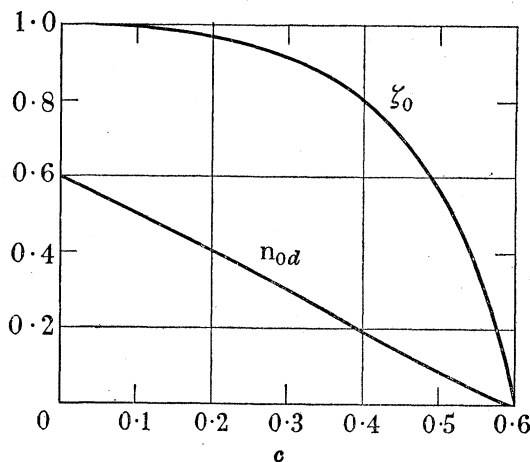


FIGURE 5. Variation of relative magnetization at absolute zero. c , fractional atomic concentration of copper. n_{0d} , effective magnetic 'carriers' per atom; $n_{0d} = \zeta_0 N_{0d}$.

The numerical values of interchange interaction parameters and related quantities, given in table 1, are, of course, dependent on the values assumed for ϵ_{0d} and θ' for nickel, and are of less significance than the general variation with copper concentration. The variation of θ' , shown graphically in figure 4, is connected with the depend-

ence of the exchange energy on the number (and so on the average distance apart) of the effectively 'interacting' particles, and raises fundamental problems to which only preliminary consideration has as yet been given.

As shown in figure 5, the relative magnetization at absolute zero, ζ_0 , decreases with the copper concentration, although ζ_0 is very near to unity for a considerable concentration range. The calculated variation of n_{0d} , the effective number of magnetic 'carriers' per atom, is approximately linear, in good agreement with the observed variation of the absolute saturation moments (Alder 1916). Independent evidence for the general character of the variation of ζ_0 with c , calculated here from experimental values of the Curie temperature, is provided by a consideration of the high-temperature susceptibility results (cf. § 4).

TABLE 1. VARIATION OF INTERCHANGE INTERACTION
COEFFICIENTS AND RELATED QUANTITIES

c , fractional atomic concentration of copper, θ , Curie temperature, °K (cf. relation (2.6) and figure 3). θ' , interchange interaction coefficient, expressed as a temperature, °K. ζ_0 , relative magnetization at 0°K. N_{0d} , number of holes per atom in the d band at 0°K. n_{0d} , effective magnetic 'carriers' at 0°K, $n_{0d} = \zeta_0 N_{0d}$. σ_0 , absolute saturation moment per gram.

c	$\theta \times 10^{-3}$	$\theta' \times 10^{-3}$	ζ_0	N_{0d}	n_{0d}	σ_0
0.00	0.6310	1.2320	1.0000	0.6000	0.6000	57.10
0.05	0.5784	1.1566	0.9972	0.5546	0.5531	52.63
0.10	0.5258	1.0804	0.9907	0.5093	0.5046	48.02
0.15	0.4732	1.0033	0.9801	0.4642	0.4550	43.30
0.20	0.4207	0.9254	0.9644	0.4192	0.4043	39.42
0.25	0.3681	0.8464	0.9419	0.3744	0.3527	33.56
0.30	0.3155	0.7662	0.9101	0.3298	0.3002	28.57
0.35	0.2629	0.6846	0.8650	0.2855	0.2469	23.50
0.40	0.2103	0.6016	0.8001	0.2414	0.1932	18.38
0.45	0.1578	0.5168	0.7051	0.1977	0.1394	13.27
0.50	0.1052	0.4299	0.5626	0.1544	0.0869	8.27
0.55	0.0526	0.3405	0.3475	0.1117	0.0388	3.69
0.60	0.0000	0.2467	0.0000	0.0698	0.0000	0.00

With the present treatment the spontaneous magnetization even at absolute zero is not necessarily equal to the absolute saturation magnetization. In favourable cases, in principle, a fairly direct experimental test would be possible. For an alloy with $c = 0.5$, for example, the relative magnetization at absolute zero would increase by about 15 % (from $\zeta_0 = 0.563$) in a field of 50,000 oersted. A change of this magnitude would be easily measured, but an unambiguous analysis of the observed change of magnetization into a part due to increase in true magnetization, and a part due to the ordinary increase of apparent magnetization, might present difficulties, which, however, should not be insuperable.

3. ELECTRON TRANSFER EFFECT IN NICKEL-COPPER ALLOYS

With increase of temperature the distribution of electrons, described in the preceding section, changes, partly owing to the movement of electrons to higher levels in the same band, and partly owing to what may be described as a transfer of electrons from the d band to the s band. The transfer is a consequence of the general

movement to states of higher energy as the temperature increases. In the d band both the energy and the number of states are limited, while in the s band, effectively, these limitations do not arise (cf. figure 1). The extent of the transfer depends strongly on the value of the band-width ratio, r_0 , and is conditioned by the equality of the partial chemical potentials in the two bands. In this section the magnitude of the effect is determined for nickel-copper alloys. It may be noted that, even if the d band is full at absolute zero (as for alloys with a copper concentration higher than $c_{\text{crit.}}$, cf. § 2), an appreciable electron transfer may still occur at higher temperatures, particularly if the energy difference between the top of the d band and the top of the Fermi distribution in the s band is small.

The general importance of the transfer effect lies in the fact that, without the introduction of any additional arbitrary assumptions, it accounts quantitatively (at least as to order of magnitude) for a number of hitherto unexplained peculiarities in the temperature variation of physical properties in both the higher and lower temperature ranges (cf. §§ 4 and 5).

(a) Theoretical discussion

The transfer effect has been discussed previously for nickel (Wohlfarth 1948), which is particularly simple, as the number of holes in the d band is equal to the number of electrons in the s band at all temperatures. For an alloy this no longer holds. For a given fractional atomic concentration of copper, c ,

$$N_{0s} - N_{0d} = N_s - N_d = c. \quad (3.1)$$

Here N_{0s} , N_{0d} refer to the number of 'particles' at absolute zero, and N_s , N_d at any temperature T . As shown in the previous paper, N and N_0 are related by

$$N = \frac{3}{2} N_0 (kT/\epsilon_0)^{\frac{3}{2}} F(\eta), \quad (3.2)$$

$$\eta = \mu/kT, \quad (3.3)$$

μ being the chemical potential (Gibbs free energy per particle, electron or hole).

Hence from (3.1)
$$\frac{3}{2} \left(\frac{kT}{\epsilon_{0s}} \right)^{\frac{3}{2}} F(\eta_s) = \frac{3}{2} \frac{N_{0d}}{N_{0s}} \left(\frac{kT}{\epsilon_{0d}} \right)^{\frac{3}{2}} F(\eta_d) + \left(1 - \frac{N_{0d}}{N_{0s}} \right), \quad (3.4)$$

where $(\epsilon_{0s})_c$, $(\epsilon_{0d})_c$ refer to the band widths for an alloy with copper concentration c , $(\epsilon_{0s})_0$, $(\epsilon_{0d})_0$ being the corresponding values for nickel. In (3.4) η_s and η_d are the statistical parameters, corresponding to the partial chemical potentials measured from the bottom of the s band and the top of the d band respectively. Using abbreviations:

$$r_0 = (\epsilon_{0s})_0/(\epsilon_{0d})_0, \quad \tau_0 = kT/(\epsilon_{0d})_0,$$

$$r_c = (\epsilon_{0s})_c/(\epsilon_{0d})_c, \quad \tau_c = kT/(\epsilon_{0d})_c,$$

(3.4) may be written as

$$F(\eta_s) = (N_{0d}/N_{0s}) r_c^{\frac{3}{2}} F(\eta_d) + \frac{2}{3} (r_c/\tau_c)^{\frac{3}{2}} (1 - N_{0d}/N_{0s}). \quad (3.5)$$

The condition for equilibrium at any temperature is the equality of the chemical potentials of the particles, measured from the same origin, say the bottom of the s band. Using (2.4) and (3.3),

$$kT\eta_s = (\epsilon_{0s})_0 + (\epsilon_{0d})_0 - kT\eta_d,$$

or, putting $\eta_d = \eta$,

$$\eta_s = (1 + r_0)/\tau_0 - \eta. \quad (3.6)$$

It follows from (3.5) and (3.6) that

$$F[(1+r_0)/\tau_0-\eta] = (N_{0d}/N_{0s})r_c^{\frac{2}{3}}F(\eta) + \frac{2}{3}(r_c/\tau_c)^{\frac{2}{3}}(1-N_{0d}/N_{0s}). \quad (3.7)$$

This equation may be obtained in a form convenient for numerical evaluation by inserting (2.1), (2.2) and (2.3). Relations are found between r_c and r_0 , τ_c and τ_0 , leading to

$$F[(1+r_0)/\tau_0-\eta] = r_0^{\frac{2}{3}}F(\eta) + \frac{10}{9}(r_0/\tau_0)^{\frac{2}{3}}c. \quad (3.8)$$

N_d is given by (3.2), which reduces to

$$N_d = 0.9\tau_0^{\frac{2}{3}}F(\eta). \quad (3.9)$$

Equations (3.8) and (3.9) reduce to those for pure nickel ($c = 0$) obtained previously. Their convenience lies in the fact that the copper concentration enters only through the last term on the right-hand side of (3.8), while τ_0 is related to the temperature in the same way as for pure nickel (i.e. τ_0 is equal to roughly $T/2000$), and r_0 may be taken to have the value 10 as before.

In the derivation outlined it is assumed that $c < c_{\text{crit.}}$, i.e. that the d band contains holes at absolute zero. It may be easily shown, however, that relations (3.8) and (3.9) hold even if the d band is full at absolute zero, thus covering the complete concentration range. For values of c approaching unity, the equations may be reduced to a classical form. In the limit

$$F(\eta) \rightarrow 0, \quad F[(1+r_0)/\tau_0-\eta] \rightarrow \infty,$$

and, after insertion of approximate values for the Fermi-Dirac integral, it is found that

$$\eta = -\Delta\epsilon/kT, \quad N_d = 0.798\tau_0^{\frac{2}{3}}\exp(-\Delta\epsilon/kT), \quad (3.10)$$

where $\Delta\epsilon$ is the energy difference between the top of the d band and the top of the Fermi distribution in the s band. Relation (3.10) is valid only for large values of the copper concentration and at low temperatures; in all other cases recourse must be made to numerical solution of the equations (3.8) and (3.9). The process of solution is here much more tedious than for nickel; a trial and error method was followed, in which the two sides of (3.8) were made to agree within the limits of accuracy aimed at (1 unit in the 6th significant figure). Three sets of results were obtained as follows:

- (1) $c = 0.352, \quad \tau_0 = 0.0(0.1) 1.0,$
- (2) $c = 0.75, \quad \tau_0 = 0.0(0.1) 1.0,$
- (3) $\tau_0 = 0.5, \quad c = 0.0(0.1) 1.0, c_{\text{crit.}}$

Sets (1) and (2) were planned as being directly applicable to the susceptibility results, due to Wheeler (1939) and Kaufmann & Starr (1943) respectively. Set (3) was obtained to determine how the magnitude of the transfer effect depends on copper concentration at one particular temperature ($\tau_0 = 0.5$, corresponding roughly to $T = 1000^\circ\text{K}$). In obtaining solutions of the equations, extensive use was made of the tables of Fermi-Dirac integrals due to McDougall & Stoner (1938).

(b) Computational results and discussion

The results of the calculations are shown in figures 6, 7 and 8, and the numerical results for set (3) are given in table 2. Figure 6 gives the results for sets (1) and (2) and shows the temperature dependence of the number of holes per atom for the

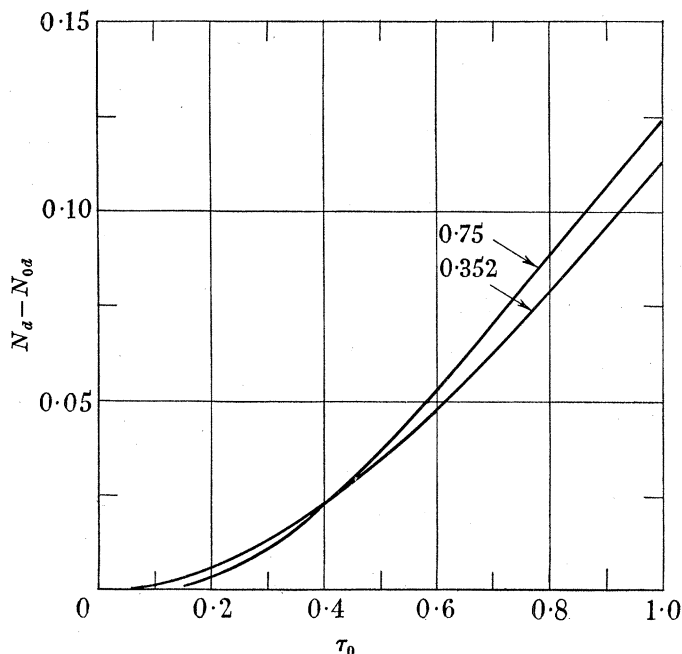


FIGURE 6. Variation of $(N_d - N_{0d})$ with temperature. N_d , N_{0d} , holes per atom at reduced temperature τ_0 and absolute zero respectively. $\tau_0 = kT/(\epsilon_{0d})_0$ referred to the unoccupied width of nickel d band. $c = 0.352, 0.75$ as indicated. $r_0 = (\epsilon_{0s})_0/(\epsilon_{0d})_0 = 10$.

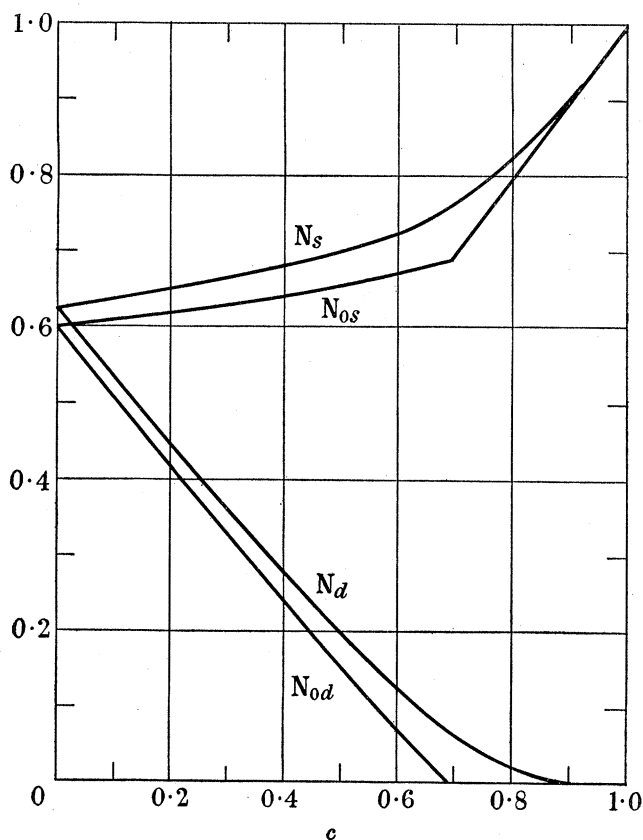


FIGURE 7. Variation of N_d and related quantities with concentration. N_d , N_{0d} , holes per atom at reduced temperature $\tau_0 = 0.5$ ($T \doteq 1000^\circ\text{K}$) and absolute zero respectively. N_s , N_{0s} , electrons per atom. c , fractional atomic concentration of copper (cf. figure 2). $r_0 = 10$.

two alloys. The values plotted represent the number of electrons per atom actually transferred from the d band to the s band for a given temperature change. For the alloy with $c = 0.352$ the d band contains 0.248 hole per atom at absolute zero and the effect amounts to as much as 40 % of N_{0d} for $\tau_0 = 1.0$. For the alloy with $c = 0.75$ the d band is full at absolute zero ($N_{0d} = 0$). The number of holes at higher temperatures is large; for $\tau_0 = 1.0$, for example, $N_d = 0.125$, amounting to about 18 %

TABLE 2. ELECTRON TRANSFER EFFECT DEPENDING ON
COPPER CONCENTRATION. $\tau_0 = 0.5$, $r_0 = 10$

c , fractional atomic concentration of copper. η , statistical parameter. $F(\eta)$, Fermi-Dirac integral. N_d, N_{0d} , holes per atom in the d band at reduced temperature τ_0 and 0°K respectively. For $c \geq c_{\text{crit}}$, $N_{0d} = 0$.

c	η	$F(\eta)$	N_d	$N_d - N_{0d}$	N_d/N_{0d}
0.0	+1.5490	1.9555	0.6222	0.0222	1.0371
0.1	1.2912	1.6782	0.5340	0.0247	1.0484
0.2	1.0090	1.4046	0.4469	0.0277	1.0661
0.3	0.6939	1.1362	0.3615	0.0317	1.0960
0.4	0.3316	0.8749	0.2784	0.0370	1.1532
0.5	-0.1026	0.6248	0.1994	0.0451	1.2919
0.6	-0.6565	0.3933	0.1251	0.0553	1.7920
0.6922	-1.3574	0.2098	0.0668	0.0668	—
0.7	-1.4292	0.1963	0.0625	0.0625	—
0.8	-2.6038	0.0639	0.0203	0.0203	—
0.9	-4.2534	0.0125	0.0040	0.0040	—
1.0	-6.0970	0.0020	0.0006	0.0006	—

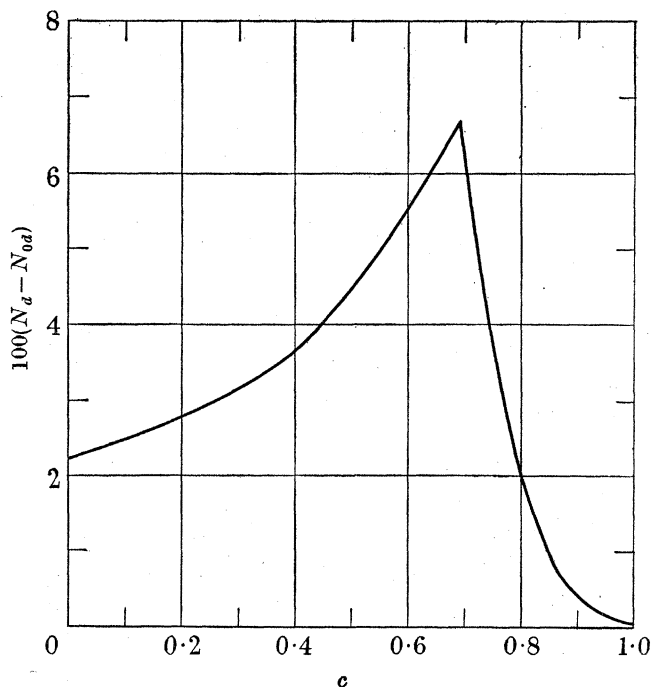


FIGURE 8. Variation of $(N_d - N_{0d})$ with copper concentration. N_d, N_{0d} , holes per atom at reduced temperature $\tau_0 = 0.5$ ($T \doteq 1000^\circ\text{K}$) and absolute zero respectively. c , fractional atomic concentration of copper. $r_0 = 10$.

of the number of holes in the d band of pure nickel at the same temperature. Corresponding values for intermediate temperatures, which are required for application to the susceptibility results (cf. § 4), are easily obtainable from the curves by graphical interpolation.

Figure 7 shows the variation of the number of particles per atom, at absolute zero and for $\tau_0 = 0.5$, for the whole composition range. At the higher temperature the change of the number of particles with c is more gradual than at absolute zero, and there is no discontinuous variation at the critical concentration. The difference between the two lower curves, $(N_d - N_{0d})$, is shown on a larger scale in figure 8, from which it appears that the magnitude of the effect increases from the value for pure nickel, $(N_d - N_{0d}) = 0.022$, to a maximum, $(N_d - N_{0d}) = 0.067$, for the alloy with the copper concentration, $c_{\text{crit.}} = 0.692$, for which the d band is just full at absolute zero. For $c > c_{\text{crit.}}$, N_d decreases rapidly, but is still quite appreciable for some 10 to 15 % beyond $c_{\text{crit.}}$, although it is negligibly small for pure copper.

4. PARAMAGNETIC SUSCEPTIBILITY OF NICKEL-COPPER ALLOYS

(a) Nickel-rich alloys. Theoretical

One of the main applications of the results obtained in the preceding sections is to paramagnetic susceptibility. For nickel-rich alloys (with more than about 40 % nickel) the Curie temperature, θ , is positive, and the alloys are paramagnetic for $T > \theta$. Theoretical susceptibility, temperature curves may be obtained in a form convenient for comparison with experimental results, using a method essentially the same as that given in I (cf. also Stoner 1938c). A 'reduced' inverse susceptibility, $(\mu_B \sigma_0 / k\theta) (1/\chi)$, is plotted against a 'reduced' temperature, T/θ , σ_0 being the absolute saturation moment per unit mass and χ the mass susceptibility. For an isolated d band, the expression for the reduced inverse susceptibility is

$$\frac{\mu_B \sigma_0}{k\theta} \frac{1}{\chi_d} = \frac{\zeta_0 \mu_B H}{\zeta k\theta}, \quad (4.1)$$

ζ_0 , ζ being the relative magnetization at 0 and $T^\circ \text{K}$ respectively. For two overlapping bands it is necessary to take account not only of the holes in the d band, but also of the s electrons, and of the effect of the electron transfer from the d band to the s band. An increase, with temperature, of the number of holes in the d band is manifested by a relative increase of mass susceptibility. It may be shown from the results of the preceding sections that the relation for mass susceptibility, appropriate to two overlapping bands, becomes

$$\frac{\mu_B \sigma_0}{k\theta} \frac{1}{\chi} = \frac{N_{0d} \zeta_0 \mu_B H}{N_d \zeta k\theta} \left/ \left(1 + \alpha \frac{\zeta_0 \mu_B H}{\zeta k\theta} \right) \right., \quad (4.2)$$

where $\alpha = (k\theta / \mu_B \sigma_0) \chi_s$, χ_s being the contribution to the mass susceptibility of the s electrons. For nickel $\epsilon_{0s} / kT \gg 1$, and χ_s may be taken to have its 'low-temperature' value,

$$\chi_s = \frac{3 \mu_B^2}{2 \epsilon_{0s}} \frac{LN_s}{A},$$

where N_s is the number of electrons per atom in the s band, L Avogadro's number and A the atomic weight. Since $\epsilon_{0s}/\epsilon_{0d}$ is large, χ_s/χ_d is small, and it may be assumed, with sufficient accuracy, that N_s remains constant for all values of concentration and temperature, the calculated value of α being about 0.02.

For the evaluation of (4.2) values of N_d/N_{0d} are required, and have been calculated for pure nickel and an alloy with $c = 0.352$ (cf. § 3). Calculations of $(\zeta_0/\zeta)(\mu_B H/k\theta)$ for a range of values of the relative magnetization at absolute zero, $0 \leq \zeta_0 \leq 1$, were carried out as follows. For a given value of ζ_0 the values of $k\theta'/\epsilon_0$ and $k\theta/\epsilon_0$ are given in I (table III). For pure nickel rough preliminary calculations showed that saturation was just complete at absolute zero, $\zeta_0 = 1$ corresponding to the critical value $k\theta'/\epsilon_0 = 2^{-\frac{1}{2}}$ (cf. (1.1)). Calculations were carried out for values of the reduced temperature

$$T/\theta = 0.00(0.05) 2.70.$$

It follows from (I, 3.8) that

$$\frac{\zeta_0 \mu_B H}{\zeta k\theta} = \frac{\zeta_0 \epsilon_0 \mu_B H}{k\theta \zeta \epsilon_0} = \frac{\zeta_0}{k\theta/\epsilon_0} \left[\frac{kT}{\epsilon_0} \frac{F(\eta)}{F'(\eta)} - \frac{k\theta'}{\epsilon_0} \right], \quad (4.3)$$

where

$$\frac{kT}{\epsilon_0} = \frac{T}{\theta} \frac{k\theta}{\epsilon_0},$$

and where

$$F(\eta) = \frac{2}{3}(kT/\epsilon_0)^{-\frac{3}{2}}.$$

Values of $(kT/\epsilon_0)(F/F')$ have been computed by Stoner (1938*d*) for equi-spaced values of the argument. Interpolations were made by a central difference method (Comrie 1936), except for $kT/\epsilon_0 \leq 0.1$, when a series expansion had to be used. The results of the computations are shown in figure 9. The curves shown are applicable to a single d band, but may be modified, through (4.2), so as to apply to two overlapping bands. A comparison is then possible with experimental results.

(b) Nickel-rich alloys. *Experimental results and discussion*

The experimental results for nickel, due to Sucksmith & Pearce (1938), have been obtained in reduced form, and are shown in figure 10 together with theoretical curves, applicable to an isolated d band (broken curve) and two overlapping bands (full curve), ζ_0 being equal to unity in both cases. It may be noted incidentally that the difference between the two theoretical curves indicates the modification introduced by a consideration of two overlapping bands, rather than of a single band. Whereas the curve for a single band is convex towards the temperature axis over the whole range (cf. I; also Stoner 1938*c*), the curve for overlapping bands is approximately linear over a wide temperature range and finally becomes slightly concave towards the temperature axis. A discussion of the agreement between the theoretical curves and the experimental results is given below.

The experimental results for five nickel-copper alloys, due to Wheeler (1939), are shown in reduced form in figure 11, together with the results for pure nickel, due to Fallot (1944). A detailed comparison with theoretical curves is possible only for the 0.352 alloy, for which results of calculations of the transfer effect are available. The experimental results for this alloy are shown separately in figure 12, together with

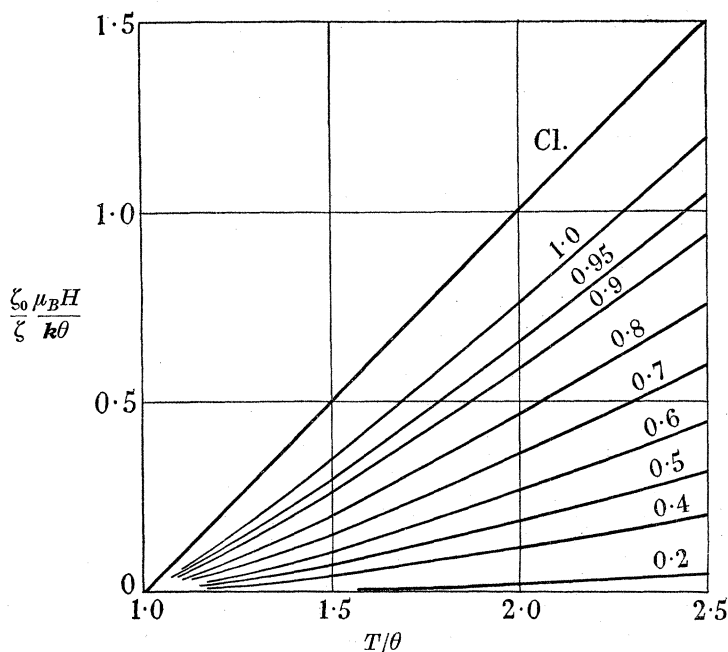


FIGURE 9. Theoretical susceptibility curves for a single band. T/θ , reduced temperature. $(\zeta_0/\zeta) (\mu_B H/k\theta)$, reduced mass susceptibility (cf. (4.1)). ζ_0 , ζ , relative magnetization at 0 and T° K respectively. Curve marked Cl. corresponds to classical statistics ($e_0/k\theta' \rightarrow 0$). Values of ζ_0 indicated.

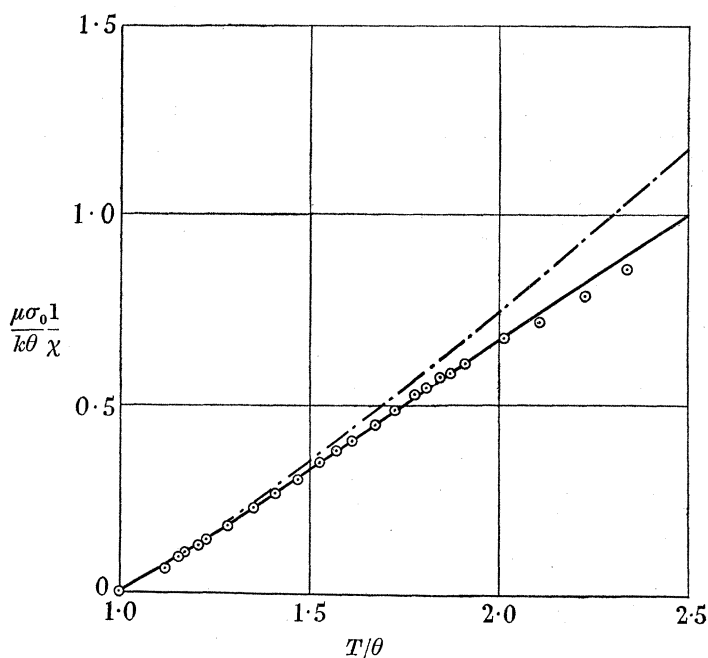


FIGURE 10. Paramagnetic susceptibility of nickel. Full curve, $r_0 = 10$. Broken curve, $r_0 \rightarrow \infty$. $\zeta_0 = 1$ (cf. figure 9). Experimental points due to Sucksmith & Pearce (1938).

theoretical curves, applicable to two overlapping bands, and with $\zeta_0 = 0.9$ and 0.8 respectively. To assess the effect of the electron transfer in this case, the two curves shown should be compared with the corresponding curves of figure 9.

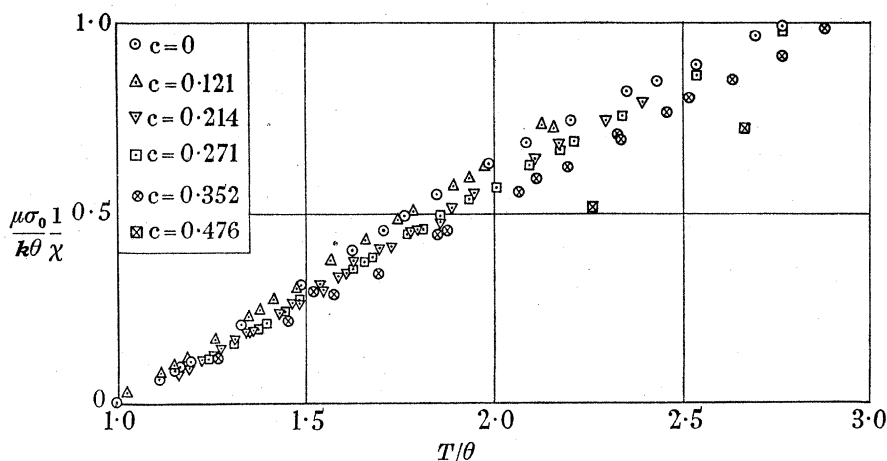


FIGURE 11. Paramagnetic susceptibility of nickel-copper alloys. Experimental results due to Wheeler (1939) (nickel-copper) and Fallot (1944) (nickel).

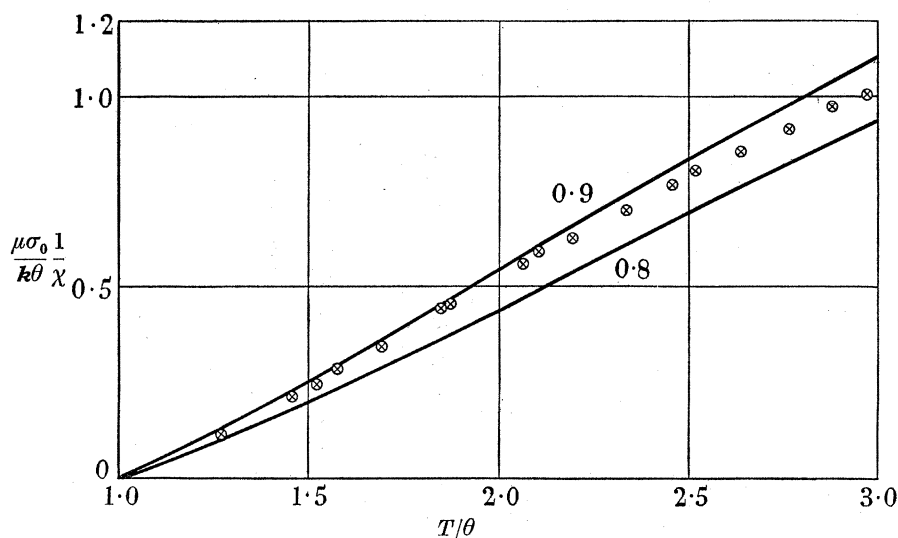


FIGURE 12. Paramagnetic susceptibility of 0.352 alloy. Curves corresponding to $r_0 = 10$, $\zeta_0 = 0.9, 0.8$. Experimental results due to Wheeler (1939).

In discussing the experimental susceptibility, temperature curves it is convenient to consider first their general course for particular alloys, and secondly the effect on the curves of varying the copper concentration. As shown in the figures, in the $1/\chi - T$ curves a curvature, concave upwards, occurs in the neighbourhood of the Curie point, followed by a sensibly linear portion, and finally, at high temperatures, by a portion which is concave towards the temperature axis. The observed behaviour at temperatures some way beyond the Curie point is covered

satisfactorily by the basic collective electron treatment. (A full discussion of the applicability of the treatment to ferromagnetics above the Curie point is given by Stoner (1948).) The interpretation of the observed high-temperature concavity of the $1/\chi - T$ curves is here based on an increase, with temperature, of the number of holes in the d band. Although this accounts for the major part of the curvature, it does not suffice to explain the whole of it, indicating that other factors, which cause a relative temperature increase of susceptibility, may be contributory to the observed behaviour. Among such factors those closely connected with the present treatment are the temperature variation of the interchange interaction parameter and of the band widths. An increase of θ' , and so a relative increase of susceptibility, is caused by the temperature variation of the number of holes in the d band. Although, according to Néel (1940), the indirect effect of thermal expansion is a temperature decrease of θ' , rough calculations, based on those given in §§ 2 and 3, indicate that, at temperatures well above the Curie point, the temperature variation of the number of interacting particles has a greater effect than the variation of the distance between them. A decrease of the band width ϵ_{0d} (due to the thermal expansion of the lattice and a consequent decrease of the overlap of wave functions in the interatomic regions) may also result in a relative temperature increase of susceptibility. Although the form of the observed susceptibility curves at high temperatures may thus be partly explicable by factors which have not been included explicitly in the present treatment, it should be borne in mind that the experimental results themselves are here less reliable. The experimental difficulties increase considerably in the higher temperature range, and the values of mass susceptibility actually measured are small, and thus subject to greater relative uncertainties. Figures 10 and 11 indicate that, although the results for nickel due to Sucksmith & Pearce and those due to Fallot are in excellent agreement up to 1100° K, they differ at higher temperatures. In view of the uncertainties, both theoretical and experimental, in the higher temperature range, the agreement between calculated and observed susceptibility curves (figures 10 and 12) is remarkably close, particularly in view of the simplifying assumptions underlying the present treatment.

Reduced experimental susceptibility results for alloys with a wide range of composition are shown in figure 11. For the highest nickel alloys it is seen that the experimental points for different alloys are very close together, while for an increasing copper concentration there is a marked shift of the points towards the temperature axis. Comparison of these results with the theoretical curves (figure 9) indicates an initial slow decrease of ζ_0 with c and a subsequent more rapid decrease. The experimental results thus lead to a variation of ζ_0 which is in excellent agreement with that derived in § 2 from the observed variation of the Curie temperature with copper concentration. Theoretical values of interchange interaction coefficients and related quantities for the alloys are shown in table 3, calculated from the values given in table 1. For the 0.352 alloy, a ζ_0 value of 0.86 is obtained, while the susceptibility results for this alloy, shown separately in figure 12, lead to a value of roughly 0.87. Similar agreement is found for the more dilute alloys. For pure nickel, in particular, figure 10 indicates that ζ_0 just equals unity, while the previous analysis (Stoner 1938c) led to a value slightly less than 1. As a result of this kind of agreement it may

be concluded, with some degree of certainty, that the calculated variation of interchange interaction with copper concentration, or, more generally, with the number of holes, is essentially correct, at least for low values of copper concentration.

TABLE 3. THEORETICAL VALUES OF INTERCHANGE INTERACTION COEFFICIENTS AND RELATED QUANTITIES

c , atomic concentration of copper. θ , Curie temperature, °K. θ' , interchange interaction coefficient, °K. ζ_0 , relative magnetization at absolute zero. (Values derived from table 1.)

c	θ	θ'	ζ_0
0	631	1232	1.00
0.124	504	1148	0.99
0.214	406	905	0.96
0.271	346	814	0.93
0.352	261	684	0.86
0.476	130	470	0.64

(c) *Copper-rich alloys*

For alloys with a high copper concentration ($c > c_{\text{crit.}}$, cf. § 2) the d band is full at absolute zero, although, as was shown in § 3, it contains holes at higher temperatures. The resulting paramagnetic susceptibility, χ_d , is determined by the number of holes in the d band at any temperature, and is roughly proportional to T^{-1} . (In this case the classical Curie law is satisfied approximately, since $kT/\epsilon_0 > 1$ at all temperatures.) To a first approximation

$$\chi_d \propto N_d/T, \quad (4.4)$$

and, since N_d increases more rapidly with T than linearly, χ_d increases with temperature. The variation of χ_d has been calculated for an alloy with a copper concentration $c = 0.75$, using values of N_d given in table 2, and employing the 'high-temperature' series (Stoner 1938*d*), which is here applicable. The results of the calculations are shown in figure 13, which also includes the contribution to the susceptibility of the s electrons, and in which temperatures are referred to $(\epsilon_{0d})_0$, the band width for pure nickel ($(\epsilon_{0d})_0/k \doteq 2000^\circ\text{K}$). Experimental results for copper-rich alloys have been obtained by Kaufmann & Starr (1943), who found that, for some alloys, their results could be represented by an empirical relation of the form

$$\chi = \alpha T + \beta + \gamma/T. \quad (4.5)$$

Values for the coefficients in (4.5) for alloys for which the relation was found to be an accurate representation of the experimental results are reproduced in table 4. The susceptibility curves for these alloys are given in the original paper and have been reproduced by Stoner (1948, figure 4.5*a*). For some of the alloys the susceptibility increases over a wide temperature range, as symbolized by the coefficient α in (4.5). The above remarks indicate that this temperature increase is due to the variation of the number of holes in the d band. Figure 13 shows that for $c = 0.75$, $d\chi/d\tau_0$ varies roughly between 0.2×10^{-6} and 0.7×10^{-6} ; for a value of 0.4×10^{-6} , $d\chi/dT$ is equal to 2×10^{-10} , which is in good agreement, as to order of magnitude,

with the coefficients α . Although the observed high-temperature increase of susceptibility of the copper-rich alloys is thus well explained, no interpretation can at present be given of their low-temperature behaviour, symbolized by the coefficients β and γ . These indicate that, over a wide temperature range, a Curie law is obeyed approximately, the susceptibilities attaining very high values near absolute zero, and increasing rapidly with nickel concentration (cf. table 4). It appears impossible to interpret this surprising behaviour of the alloys on the basis of the treatment

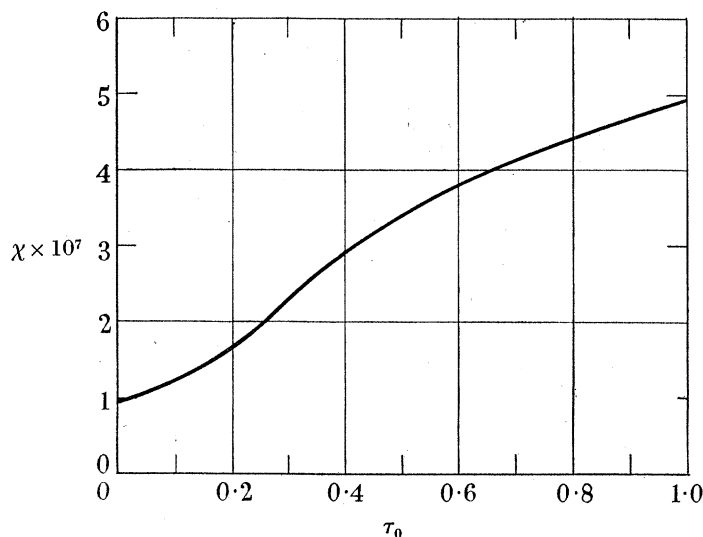


FIGURE 13. Paramagnetic susceptibility for 0.75 alloy. Values calculated for holes in the d band ($r_0 = 10$), χ_d , and for s electrons, χ_s . $\tau_0 = kT/(e_0 a)_0$, referred to nickel. $\chi = \chi_d + \chi_s$, mass susceptibility.

TABLE 4. TEMPERATURE COEFFICIENTS OF SUSCEPTIBILITY
FOR COPPER-RICH ALLOYS

c , fractional atomic concentration of copper. α , β , γ , coefficients given by Kaufmann & Starr (1943). $\chi = \alpha T + \beta + \gamma/T$, mass susceptibility.

c	$\alpha \times 10^{10}$	$\beta \times 10^6$	$\gamma \times 10^6$
0.882	1.38	0.160	6.34
0.784	2.22	0.444	13.29
0.683	0.91	1.073	51.95
0.625	0.31	1.302	197.7

outlined in the present paper. It may be that in some of these alloys the nickel atoms are not evenly distributed throughout the sample, but form small ferromagnetic 'islands' in the surrounding copper-rich matrix. Regarding γ in (4.5) as a Curie constant, Kaufmann & Starr calculated effective Bohr magneton numbers and obtained values about ten times smaller than that of pure nickel. If nickel-rich islands are responsible for the observed behaviour of the alloys, these values are indicative of the fraction of undissolved nickel which is required to simulate the observed effect.

5. ELECTRONIC HEAT OF NICKEL AND NICKEL-COPPER ALLOYS

In view of the previous detailed discussions of the electronic heat of ferromagnetics at high and low temperatures (II; cf. also Stoner 1936, 1938*b*, 1948), it will be sufficient, in this section, to examine only the present developments of the theoretical treatment in their bearing on thermal properties.

(a) *Electronic heat above the Curie point*

The expressions (Stoner 1938*b*) for the internal energy and specific heat of 'particles' with a standard energy distribution and zero intrinsic magnetization are

$$\frac{E}{N\epsilon_0} = \tau_0 \frac{F_{\frac{3}{2}}(\eta)}{F_{\frac{1}{2}}(\eta)} = \Phi(\tau_0), \quad (5.1)$$

$$C/Nk = \Phi' = d\Phi/d\tau_0, \quad (5.2)$$

where N is the number of particles and ϵ_0 the relevant band width, τ_0 being equal to kT/ϵ_0 . $F_{\frac{1}{2}}(\eta)$ and $F_{\frac{3}{2}}(\eta)$ are standard Fermi-Dirac integrals, which, for a single band, are functions of τ_0 through the relations

$$F_{\frac{3}{2}}(\eta) = \frac{2}{3}\tau_0^{-\frac{3}{2}} = \frac{2}{3} \frac{d}{d\eta} F_{\frac{1}{2}}(\eta). \quad (5.3)$$

For two overlapping bands the increase of the number of holes in the d band, due to the electron transfer discussed in §3, leads to a modification of the relations (5.1) and (5.2). It may easily be shown that the expressions become

$$E_1/N_{0d}\epsilon_{0d} = \nu^{\frac{1}{2}}\Phi(\tau_0), \quad (5.4)$$

$$C_1/N_{0d}k = \nu^{\frac{1}{2}}\Phi' + \frac{5}{3}\nu^{\frac{3}{2}}\Phi\nu', \quad (5.5)$$

where E_1 and C_1 are the modified values of energy and specific heat, N_{0d} the number of holes per atom in the d band at absolute zero, N_d at any temperature T , ϵ_{0d} the unoccupied energy width, and where $\tau_0 = kT/\epsilon_{0d}$, $\nu = N_d/N_{0d}$ and $\nu' = d\nu/d\tau_0$. The increase of specific heat due to the transfer effect has been calculated for nickel, for which values of ν had been obtained previously (Wohlfarth 1948). The values of the derivative, ν' , calculated directly from the expressions (3.8) and (3.9) (with $c = 0$), are given by

$$\nu' = \frac{3}{2} \left[\frac{\nu}{\tau_0} - \frac{1}{\tau_0^{\frac{3}{2}}} \frac{(1+r_0) F' \{ (1+r_0)/\tau_0 - \eta \}}{r_0^{\frac{3}{2}} + F' \{ (1+r_0)/\tau_0 - \eta \} / F'(\eta)} \right], \quad (5.6)$$

where $F = dF_{\frac{1}{2}}(\eta)/d\eta$, and where r_0 , the band-width ratio $\epsilon_{0s}/\epsilon_{0d}$, is taken equal to 10 as before. Values of Φ and Φ' have been tabulated by Stoner (1938*b*) for equispaced values of τ_0 , intermediate values being obtained by direct interpolation. The calculated specific heats are most appropriately expressed in practical units, cal.deg.⁻¹mol.⁻¹. Figure 14 shows the theoretical variation of specific heat above the Curie point for nickel, the curve marked C being that obtained with the previous relation (5.2), and the curve marked C' that computed for two overlapping bands from (5.5). Figure 14 does not include the discontinuity at the Curie point and the observed tailing some 20° or 30° above θ , which have been fully discussed by Néel, Stoner and others. The additional contribution to the electronic heat, due to

the temperature increase of the number of holes in the d band, is seen to be quite marked. This is mainly due to the fact that, although ν may differ relatively little from unity, the temperature derivative, ν' , may be quite large. (For $\tau_0 = 0.635$, for example, $\nu - 1 = 0.0601$, and $\nu' = 0.188$.) It is apparent from figure 14 that over a wide temperature range ($0.4 < \tau_0 < 0.8$, corresponding approximately to $800^\circ < T < 1600^\circ \text{K}$) the variation of C' is approximately linear; with $r_0 = 10$, $dC'/dT \doteq 1.18 \times 10^{-3} \text{ cal.deg.}^{-2} \text{ mol.}^{-1}$. For values of r_0 larger than 10 the electronic heat curve C' will be correspondingly less steep than that shown in the figure.

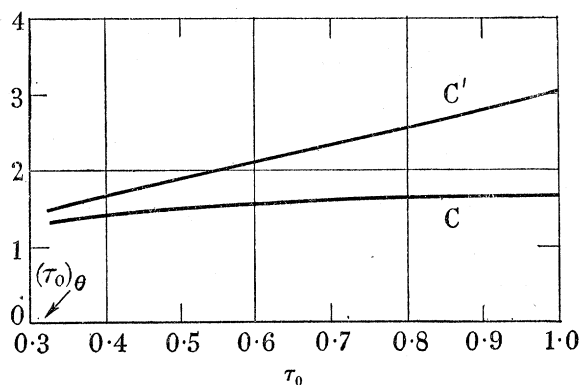


FIGURE 14. Electronic heat of nickel above the Curie point. C , C' , electronic heat due to single d band and two overlapping bands respectively. $r_0 = \epsilon_{0s}/\epsilon_{0d} = 10$. τ_0 , reduced temperature, kT/ϵ_{0d} ; $(\tau_0)_\theta$, reduced temperature corresponding to Curie point. Units: $\text{cal.deg.}^{-1} \text{ mol.}^{-1}$.

Comparison with experiment is made difficult by the paucity of reliable observational data for the temperature region of interest (i.e. from above the Curie point (631°K) to the melting-point (1725°K)). The results of Sykes & Wilkinson (1938) for nickel, which are probably the most reliable, extend only to 900°K . The results of Klinkhardt (1927) extend to 1100°K and agree well with the later results over the overlapping temperature range. Subtracting the contributions to the specific heat from the lattice vibrations (Debye term) and the dilatation, and assuming the anharmonicity correction to be negligible, the value obtained for the electronic heat at 1000°K is 1.70. This is intermediate between the theoretical value calculated from (5.2), $C = 1.50$, and the value calculated for two overlapping bands, with $r_0 = 10$, $C' = 1.90 \text{ cal.deg.}^{-1} \text{ mol.}^{-1}$. Klinkhardt's results indicate that over a restricted temperature range ($950^\circ < T < 1100^\circ \text{K}$) the electronic heat increases roughly linearly with temperature, dC/dT being about 1.5×10^{-3} . This agrees well, as to order of magnitude, with the value derived from figure 14. By adjusting the band width ratio, r_0 , better agreement could be obtained with these particular experimental results, but no great weight could be attached to an estimate of r_0 arrived at in this way.

The high-temperature specific heat for nickel-copper alloys has been measured by Grew (1934). For these alloys the tailing above the Curie point extends to very much higher temperatures, up to, and, for some alloys, beyond the highest investigated. (For an alloy with a copper concentration 0.212, with $\theta = 410^\circ \text{K}$, the

excess specific heat above the Curie point does not attain a minimum till 550° K, the highest temperature covered being 570° K.) The experiments, therefore, do not provide data to which the present analysis can be usefully applied.

(b) *Low-temperature electronic heat*

Experimental specific heat results in the helium-hydrogen temperature range are usually expressed in the form

$$C_v = \gamma T + bT^3,$$

where the first term corresponds to the electronic heat, C , and the second, to that due to lattice vibrations (Debye term). The relation for C , for 'particles' distributed in an energy band of standard form and having a resultant relative magnetization, ζ_0 , at absolute zero, is (cf. II, (4.14), (4.18))

$$\left. \begin{aligned} C/Nk &= f_1(\zeta_0) kT/\epsilon_0, \\ f_1(\zeta_0) &= \frac{1}{4}\pi^2\{(1+\zeta_0)^{\frac{1}{2}} + (1-\zeta_0)^{\frac{1}{2}}\}, \end{aligned} \right\} \quad (5.7)$$

the electronic energy being given by (cf. I, (5.10); II, (4.12))

$$\left. \begin{aligned} E/N\epsilon_0 &= 0.3f_2(\zeta_0), \\ f_2(\zeta_0) &= \{(1+\zeta_0)^{\frac{3}{2}}(1+\zeta_0/6) + (1-\zeta_0)^{\frac{3}{2}}(1-\zeta_0/6)\}. \end{aligned} \right\} \quad (5.8)$$

For paramagnetics, $\zeta_0 = 0$, and the relations reduce to the well-known forms

$$C = \frac{1}{2}\pi^2 Nk(kT/\epsilon_0), \quad E = 0.6N\epsilon_0. \quad (5.9)$$

For ferromagnetics the calculation of the low-temperature electronic heat necessitates a knowledge of ζ_0 . For nickel and nickel-copper alloys this information is provided by the calculations (§ 2) leading to the values given in table 1. Account must also be taken of the transfer effect; although the actual transfer is negligibly small at low temperatures, the variation with temperature produces an appreciable effect on the linear temperature coefficient, γ (of the order of 10 % of the whole), and has to be taken into consideration. For an application to nickel-copper alloys it is necessary to derive a low-temperature series expression for the transfer effect. It is found that, for $kT/(\epsilon_{0d})_c \ll 1$,

$$\left. \begin{aligned} \nu &= \frac{N_d}{N_{0d}} = 1 + a \left\{ \frac{kT}{(\epsilon_{0d})_c} \right\}^2, \\ \text{where } a &= \frac{\pi^2}{8r_0} \frac{(1+r_0)}{(1+c_s/0.6)^{\frac{3}{2}} + r_0(1+c_s/0.6)^{\frac{1}{2}}(1-c_d/0.6)^{\frac{1}{2}}}, \end{aligned} \right\} \quad (5.10)$$

and where N_{0d} is the number of holes per atom in the d band at absolute zero, N_d at temperature T , $(\epsilon_{0d})_c$ the unoccupied energy width of the d band for an alloy with copper concentration c , r_0 the band-width ratio for pure nickel, and where c_s and c_d are the quantities, defining the distribution of electrons at absolute zero, given by (2.1). Relation (5.10) holds for all values of the concentration approaching $c_{\text{crit.}}$ (For $c = 0.65$, for example, $kT/(\epsilon_{0d})_c = 0.1$ at 20° K.) For $c \gg c_{\text{crit.}}$, when the d band is full at absolute zero, there is no simple relation for the transfer effect at low temperatures, nor, indeed, for the electronic heat.

Relations have been obtained for computing values of γ , including contributions due to the electron transfer and to the s electrons. It is found that, for $r_0 = 10$,

$$\begin{aligned} \gamma_d \times 10^4 &= 9.104(0.6 - c_d)^{\frac{1}{3}} \{f_1(\zeta_0) + af_2(\zeta_0)\}, \\ \gamma_s \times 10^4 &= 4.492(0.6 + c_s)^{\frac{1}{3}}, \quad \gamma = \gamma_d + \gamma_s, \end{aligned} \quad (5.11)$$

where $f_1(\zeta_0)$, $f_2(\zeta_0)$ and a have been defined in (5.7), (5.8) and (5.10), and where γ is expressed in cal.deg.⁻²mol.⁻¹. The cube-root terms in (5.11) arise naturally from the assumption of a standard distribution of states, the electronic heat being directly proportional to the number of particles and inversely to the energy widths (cf. (2.1), (2.3), (5.7)). Values of the various quantities required for evaluation of (5.11) are given in § 2. With the particular value of $\zeta_0 = 1$ for pure nickel, for small values of

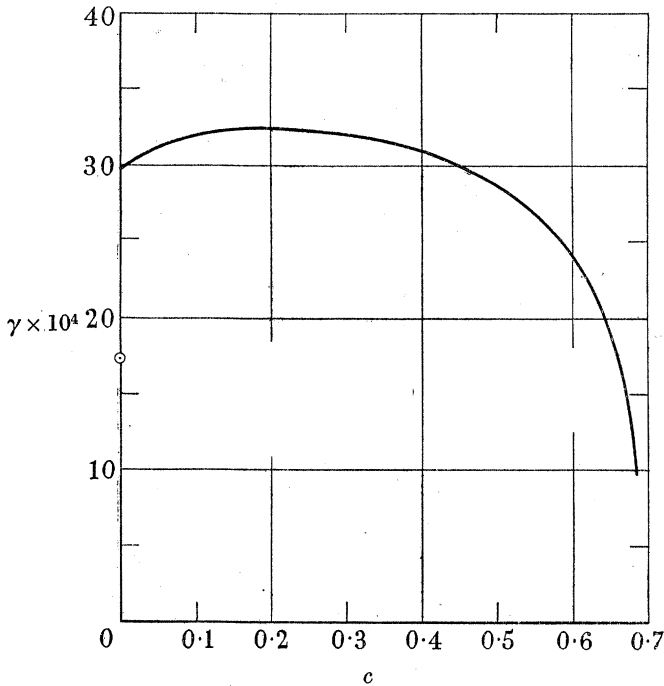


FIGURE 15. Low-temperature electronic heat of nickel-copper alloys. c , atomic concentration of copper. γ , linear temperature coefficient of specific heat, cal.deg.⁻²mol.⁻¹. Experimental points due to Keesom & Clark (1935), Keesom & Kurrelmeyer (1940).

copper concentration, $f_1(\zeta_0)$ increases rapidly with c . (For $c = 0.0$, $f_1(\zeta_0) = 3.109$, while for $c = 0.2$, $f_1(\zeta_0) = 3.902$, the maximum value, $f_1(0)$, being $\frac{1}{2}\pi^2 = 4.935$.) Since the term $(0.6 - c_d)^{\frac{1}{3}}$ drops off very slowly for small values of c , γ increases slightly (up to $c = 0.2$), and then remains approximately constant over a wide range of copper concentrations, finally decreasing rapidly as $c \rightarrow c_{\text{crit}}$, when the cube-root term becomes predominant. Theoretical values of γ are shown in figure 15, together with experimental results due to Keesom & Clark (1935) (nickel) and Keesom & Kurrelmeyer (1940) (nickel-copper alloys). The absolute discrepancy shown in figure 15 is due in the main to the difference between the values of the band width as estimated from low- and high-temperature data (cf. § 2; II, § 7). In the

evaluation of (5.11) the numerical values used are derived from the magnetic results, implying the 'high-temperature' value for the degeneracy temperature of nickel, $\epsilon_{0d}/k = 1.6 \times 10^3$ °K, rather than the 'low-temperature' value, 2.4×10^3 °K, and leading to calculated values of γ for nickel and nickel-copper alloys which are larger than those observed. Apart from this discrepancy there is very good qualitative agreement between the theoretical and experimental results; it is seen that in both cases γ remains approximately constant over a very extended range of copper concentrations. Minor deviations between the two curves, especially the initial slight increase of γ in the calculated, as compared with the slight decrease in the experimental curve, are due to uncertainties on both the theoretical and practical sides, and are of no fundamental significance. The general agreement is the more satisfactory in view of the difficulties of explaining the observed variation on any of the previous theoretical treatments (Stoner 1948), the present interpretation proceeding in an unforced way from the basic collective electron treatment given in II.

Apart from the nickel-rich alloys, Keesom & Kurrelmayer (1940) also investigated an alloy with about 80 % copper and obtained a value about 2.5 times that of pure copper (Keesom & Kok 1936). No explanation of this result can be given if the electronic heat is due entirely to s electrons, with an energy distribution of the same general type as that considered. As already pointed out (§ 4), the present treatment is inapplicable in detail to copper-rich alloys, possibly owing to an uneven distribution of nickel atoms. Nickel-rich nuclei could produce abnormally high values of specific heat, besides leading to the peculiar magnetic behaviour observed by Kaufmann & Starr (1943).

6. GENERAL DISCUSSION

The aim in this paper has been to examine in some detail the experimental results for particular substances, nickel and nickel-copper alloys, in the light of the collective electron treatment developed in I and II. The basic formulae and numerical results previously obtained are strictly applicable when there is either a single incomplete electron energy band of standard form or two (or more) overlapping bands in each of which the number of electrons is independent of temperature over the relevant range. In general, however, with overlapping bands, the number of electrons in each band varies with temperature, and the main extension of the basic treatment introduced in the present paper is in the development of a method for determining the equilibrium distribution of electrons (of given total number) between bands as well as in each single band (§ 3).

With the band form assumed (figure 1), the parameters specifying the band widths and interchange interaction can be estimated in a straightforward way from a limited range of observational data (§ 2). It is then shown that, with the limited number of specifying parameters so obtained, and taking into account the transfer effect, there is good general agreement between calculated and observed values of magnetic susceptibility and electronic heat over the whole temperature range investigated, and, in the alloys, over a wide range of composition. The agreement is not, of course, perfect. Since the specifying parameters have been estimated

essentially from high-temperature data, it is not surprising that the most marked discrepancy is that between the absolute values of the observed and calculated electronic heats near absolute zero (figure 15). The disagreement here, and the absence of 'perfect' agreement elsewhere, can be attributed, at least in part, to an oversimplification in the band form adopted, and to the non-inclusion in the theoretical treatment of some of the recognized determining factors, notably the effect of thermal expansion in modifying the band structure and interchange interaction. It may be noted, too, that imperfect agreement is not to be attributed entirely to shortcomings in the theoretical treatment; for analysis and intercomparison of the data obtained in various investigations have shown that some of the experimental values are much more uncertain than the stated, or implied, experimental errors would suggest.

The detailed quantitative discussion has been confined to the single-alloy system, nickel-copper, and since this may suggest a narrow limitation of the field of application of the general method, it is appropriate, in concluding this paper, to refer very briefly to other nickel alloys, which have been considered in a preliminary way. Fortunately, a wealth of experimental information is available on the magnetic properties (though not on specific heats) of these alloys. The saturation moments, as dependent on the concentration of the added metal in nickel, have been measured for a large number of alloys by Sadron (1932), and the Curie temperatures by Marian (1937). In addition, Manders (1936) has made a very extensive investigation of the paramagnetic susceptibilities of nickel alloys above the Curie point. It must suffice here to give the tentative conclusions drawn from a preliminary analysis of these three sets of data on the lines indicated in §§ 2 and 4.

The alloys may be regarded as falling roughly into two classes (cf. Auwers 1937; Néel 1940). First, there are the alloys in which the added metal has a small, usually constant, paramagnetism, which may be attributed to incomplete outer groups of *s* or *p* electrons. Among the nickel alloys of this class, investigated by Manders, are those with gold, zinc, aluminium, tin and antimony. It might be anticipated that the magnetic behaviour of these alloys would be somewhat similar to that of nickel-copper, the above metals adding respectively 1, 2, 3, 4 and 5 electrons to the *d* band of nickel, but that there would be an increasing divergence from the theoretical results based on that assumption with increasing valency of the added element. The analysis of the experimental results indicates, however, that the reduced susceptibility, temperature curves have characteristics very similar to those for nickel-copper (cf. figure 11). In addition, the results of Sadron and Marian show that both the saturation moments and the Curie temperatures of these alloys decrease roughly linearly with concentration over the range of solid solubility, either vanishing or extrapolating to zero, at an approximate atomic concentration $0.6/n$, n being the valency of the added metal. These results confirm the conclusions which had been reached previously as to the apparent simplicity of the magnetic properties of alloys of this class.

Alloys in the second class include those of nickel with the strongly paramagnetic transition metals, which have characteristics due to an incomplete *d* band. Among alloys considered were those with chromium, manganese, palladium and platinum.

The results of the analysis are here more interesting though more difficult to interpret, owing to uncertainties regarding the effects of the added metal in modifying the band structure of nickel. It is surprising that, even for these alloys, the observed Curie temperatures and saturation moments decrease, in the majority of cases, roughly linearly with the atomic concentration of the solute metal. Two exceptions are nickel-palladium and nickel-manganese; for the last the saturation moment increases initially with manganese concentration. The reduced susceptibility temperature curves have the same general characteristics as for nickel-copper. Deviations in detail are, however, found, and are significant. For most nickel alloys difficulties arise due to the limited range of solid solubility. For some of the alloys the results obtained are markedly dependent on heat treatment, and the Curie points and the susceptibilities are both very uncertain. In these cases a detailed analysis becomes impossible. It seems clear, however, that the characteristics of these alloys are consistent with the scheme developed in this paper, and that a more detailed analysis of the experimental results in the light of the collective electron treatment is likely to provide valuable information about band forms and interchange interaction in metals and alloys.

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Large elastic deformations of isotropic materials.

V. The problem of flexure

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A cuboid of highly elastic incompressible material, whose stored-energy function W is a function of the strain invariants, has its edges parallel to the axes x , y and z of a rectangular Cartesian co-ordinate system. It can be bent so that: (i) every plane, initially normal to the x -axis, becomes part of the curved surface of a cylinder whose axis is the z -axis; (ii) every plane, initially normal to the y -axis, becomes a plane containing the z -axis; (iii) there is no displacement parallel to the z -axis.

It is found that such a state of flexure can be maintained by the application of surface tractions only, and these are calculated explicitly in terms of the derivatives of W with respect to the strain invariants. The surface tractions are normal to the surfaces on which they act, in their deformed state. Those acting on the surfaces initially normal to the x -axis are uniform over each of these surfaces.

The assumption is then made that the stored-energy function W has the form, originally suggested by Mooney (1940), for rubber,

$$W = C_1(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_2(\lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 + \lambda_1^2\lambda_2^2 - 3),$$

where C_1 and C_2 are physical constants for the material and λ_1 , λ_2 , λ_3 are the principal extension ratios. For this case—and therefore for the incompressible neo-Hookean material (Rivlin 1948*a, b, c*), which is obtained from this by putting $C_2 = 0$ —it is found that the flexure can be maintained without the application of surface tractions to the curved surface, provided that

$$2(a_1 - a_2)(r_1 r_2)^{\frac{1}{2}} = r_1^2 - r_2^2,$$

where $(a_1 - a_2)$ is the initial dimension of the cuboid, parallel to the x -axis, and r_1 and r_2 are the radii of the curved surfaces.

When this condition is satisfied, the system of surface tractions applied to a boundary initially normal to the y -axis is equivalent to a couple M , proportional to $(C_1 + C_2)$. It is also found that the surface tractions applied to a boundary normal to the z -axis has a resultant F_z proportional to $(C_1 - C_2)$.

1. INTRODUCTION

The problem of flexure has, throughout the history of the mathematical theory of elasticity, attracted considerable attention. It has, however, generally been treated on the assumption that the material of the body considered is intrinsically only slightly elastically deformable. In spite of this it has long been recognized that the displacements undergone by the various points of the body may nevertheless be large.